

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number
WO 01/60515 A2

(51) International Patent Classification⁷: **B01J 37/00**

(21) International Application Number: **PCT/US01/05109**

(22) International Filing Date: 16 February 2001 (16.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/183,576 18 February 2000 (18.02.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

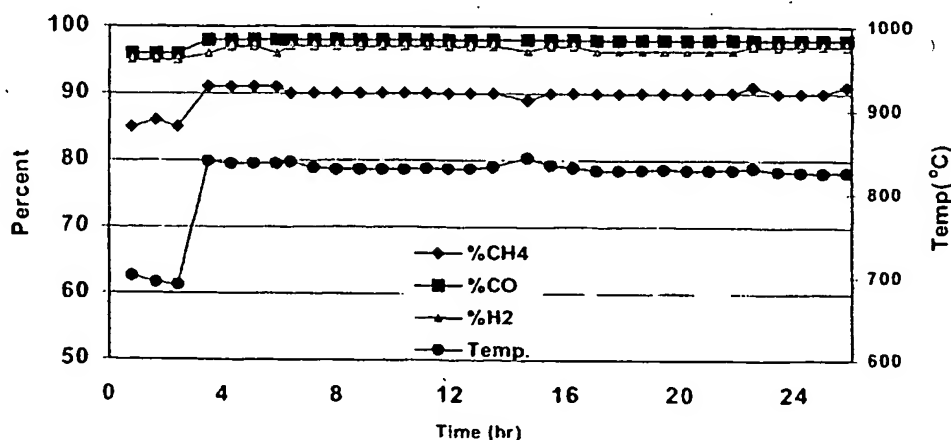
(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **RETICULATED CERAMIC FOAM CATALYSTS FOR SYNTHESIS GAS PRODUCTION**



(57) Abstract: Reticulated ceramic monolithic catalysts and non-poisoning catalyst supports comprising one or more metal oxides of chromium, cobalt, nickel, an alkaline earth, a rare earth, or another sinterable metal oxide that are active in any of various chemical oxidation reactions are disclosed. Methods of making the new reticulated ceramic structures comprising impregnating an organic foam or other pore-templating material are also disclosed. Processes for the catalytic conversion of light hydrocarbons to products comprising carbon monoxide and hydrogen employing reticulated ceramic catalysts are described.

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RETICULATED CERAMIC FOAM CATALYSTS FOR SYNTHESIS GAS PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. 119(e) of U.S. Provisional
5 Application No. 60/183,576 filed February 18, 2000.

BACKGROUND OF THE INVENTION

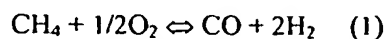
Field of the Invention

The present invention generally relates to catalysts for converting light hydrocarbons
(e.g., methane) to products containing carbon monoxide and hydrogen (synthesis gas).
10 More particularly, the invention relates to macroporous monolithic self-supported active
catalyst structures and to non-poisoning catalyst support structures having a high surface-
area-to-volume ratio.

Description of Related Art

The catalytic partial oxidation of light hydrocarbons, such as C₁-C₅ hydrocarbons, to
15 yield products containing a mixture of carbon monoxide and hydrogen ("synthesis gas" or
"syngas") is currently an area of intense interest and investigation. Much of the work in this
field has been described in the literature. One focal point of this research is on methane; the
main component of natural gas, as a starting material for the production of higher
hydrocarbons and hydrocarbon liquids in order to improve the economics of natural gas use.
20 This is due to the fact that there is a great deal of natural gas available in many areas of the
world, and the world's natural gas supply is predicted to outlast the world's oil reserves by a
significant margin. Most of the world's natural gas supply is situated in areas that are
geographically remote from population and industrial centers, however. The costs of
compression, transportation, and storage make the commercial use of natural gas
25 economically unattractive. At the present time, commercial production of synthesis gas by
methane conversion primarily utilizes steam reforming processes, which result in a similar
gas product mixture to that obtained by partial oxidation of methane. Conventional steam
reforming processes are well described in the literature.

In catalytic partial oxidation processes the gaseous hydrocarbon feedstock is mixed
30 with air, oxygen-enriched air, or oxygen, and introduced to a catalyst at elevated
temperature and pressure. The partial oxidation of methane yields a syngas mixture with a
H₂:CO ratio of 2:1, as shown in Equation 1.



This product ratio is especially desirable for such downstream applications as the conversion of the syngas to methanol, or conversion to hydrocarbon products such as fuels boiling in the middle distillate range (e.g. kerosene and diesel fuel) and hydrocarbon waxes by processes such as the Fischer-Tropsch Synthesis. The partial oxidation of methane is an exothermic reaction and proceeds at a faster rate than the older steam reforming processes for producing syngas. Shorter catalyst contact times and reduced scale reactors to accomplish partial oxidation of a hydrocarbon feedstock are some of the improvements made possible by a catalytic partial oxidation process.

The selectivities of catalytic partial oxidation to the desired products, carbon monoxide and hydrogen, are controlled by several factors, but one of the most important of these factors is the choice of catalyst composition. Typically, the best catalyst compositions have included precious metals and/or rare earths. The large volumes of expensive catalysts needed by typical catalytic partial oxidation processes have placed these processes generally outside the limits of economic justification, however. For successful operation at commercial scale, the catalytic partial oxidation process must be able to achieve a high conversion of the methane feedstock at high gas hourly space velocities (GHSV), and the selectivity of the process to the desired products of carbon monoxide and hydrogen must be high. Such high conversion and selectivity must be achieved without detrimental effects to the catalyst, such as the formation of carbon deposits ("coke") on the catalyst, which severely reduces catalyst performance. Accordingly, substantial effort has been devoted to the development of highly active catalysts allowing commercial performance without coke formation.

A number of process regimes have been described in the literature for the production of syngas via catalyzed partial oxidation reactions. The noble metals, which typically serve as the best catalysts for the partial oxidation of methane, are scarce and expensive. The widely used, less expensive, nickel-based catalysts have the disadvantage of promoting coke formation on the catalyst during the reaction, which results in loss of catalytic activity. Moreover, in order to obtain acceptable levels of conversion of gaseous hydrocarbon feedstock to CO and H₂ it is typically necessary to operate the reactor at a relatively low flow rate, or gas hourly space velocity, using a large quantity of catalyst.

U.S. Pat. No. 4,810,685 (assigned to Imperial Chemical Industries PLC) discloses certain steam reforming catalysts containing strong ceramic foams comprising at least 50% by weight, of oxides of Fe, Co, Ni, Cu, Va, Mo, W, Cr, Mn or Zn. EPO 303,438 (assigned to Davy McKee Corporation) describes certain syngas catalysts that provide surface area to

volume ratio of $5 \text{ cm}^2/\text{cm}^3$ to about $40 \text{ cm}^2/\text{cm}^3$. For example, high surface area alumina is deposited on a honeycomb monolith of cordierite material to serve as a support upon which finely dispersed catalytic metal components such as Pt and Pd are distended.

U.S. Pat. No. 5,648,582 (assigned to Regents of the University of Minnesota)
5 discloses a process for the catalytic partial oxidation of methane at space velocities of 800,000 to 12,000,000 hr^{-1} on certain Rh, Ni and Pt catalysts supported by a ceramic monolith. The small catalyst bed used in this process is said to eliminate hot spots which are typical of relatively thick catalyst beds.

Short contact time, reduced scale catalytic partial oxidation processes for producing
10 syngas from methane require highly active catalysts and support structures that can function for a long period of time under the required high temperature and high pressure operating conditions. Most supported catalysts with good activity and high porosity tend to break down rapidly on-stream, however. Another problem that is encountered in many methane oxidation processes employing supported catalysts is that the porous support "poisons" the
15 active catalyst. The poison is a component that is not present on the active catalyst overlayer and which affects catalyst performance in some way. In many cases, the poison interferes with the performance of the catalyst. Chemical interactions between the oxides of the group VIII transition metals and the reactive components of the support lead to the formation of catalytically inactive binary oxide phases. The catalytic phase purity is
20 disrupted, or poisoned. For example, nickel forms nickel aluminate over an α -aluminate support. Some catalyst structures employ diffusion barriers between the active catalyst and the support structure in an attempt to ameliorate this problem.

Others have described processes pertaining to the sintering of chromium oxide, but the resulting sintered chromium oxide products are not suitable structures for use as syngas
25 generation catalysts. For example, T. Li, et al. (1999 *J. Eur. Ceram. Soc.* 19:399-405) discloses a method of sintering Cr_2O_3 in $\text{H}_2/\text{H}_2\text{O}$ gas mixtures. M. Li, et al. (1998 *China's Refract.* 7:11-13) describes a key technique of manufacture of dense chromium sesquioxide refractories. S. Hashimoto, et al. (1996 *J. Ceram. Soc.* 104:1121-1124) describes densely sintered, compacted MgO and Cr_2O_3 powders. M. Yoshinaka, et al. (1995 *J. Am. Ceram.*
30 *Soc.* 78:2271-3) describe a hot isostatic pressed sol-gel derived chromium (III) oxide. A. Harabi, et al. (1995 *Br. Ceram. Trans.* 94:97-102) describe densification and grain growth in sintered alumina-chromia powder mixtures. Loss of chromia was substantial in compacts with more than 10 wt% chromia. U. Balachandran et al. (1995 *Nanostruct. Mater.* 5:505-

12) describe the synthesis, sintering and magnetic properties of a nanophase Cr_2O_3 composition. R. Waesche, et al. (1995 *Ceram. Trans.* 51:531-5) describe the sintering and characterization of certain gelcast alumina-chromia reaction bonded ceramics. T. Li, et al. (1995 *Ceram. Trans.* 51:231-5) describes a process for making reaction-bonded Cr_2O_3 ceramics.

What is needed are economical, yet highly active catalyst structures that permit short contact time and high flow rates on stream without causing excessive back pressure and without deteriorating under operational temperature and pressure conditions. Superior syngas catalysts, for example, need to possess macroporosity (to minimize back pressure), thermal heat resistance and mechanical strength for use at high volumetric flow rates. The catalyst should also be free of interfering chemical interactions with the support material.

SUMMARY OF THE INVENTION

Conventional catalysts or catalyst support structures, particularly those employed for catalyzing the conversion of light hydrocarbons (such as methane) to synthesis gas, do not include free standing Cr oxide foams or reticulated ceramics. The active catalyst structures, catalyst supports and syngas production methods of the present invention are able to overcome some of the shortcomings of previous catalysts and syngas production processes by permitting short contact time of the reactant gases with the catalyst bed, and allowing high flow rates of reactant and product gases. Due to the favorable structure of the catalyst, or catalyst support, this is accomplished without causing excessive back pressure. The new catalysts and supports resist deterioration under operational temperature and pressure conditions better than typical catalysts in use today for syngas production. The preferred new catalysts comprise reticulated ceramic structures, preferably ceramic foams, and demonstrate excellent levels of conversion of methane and oxygen reactants and selectivities for CO and H_2 products by a predominantly, or net partial oxidation reaction.

According to certain embodiments, the reticulated foam catalyst contains one or more metal oxides of chromium, cobalt, nickel, an alkaline earth, a rare earth, or another sinterable metal oxide that is active in any of various chemical oxidation reactions, preferably the catalytic partial oxidation of methane to synthesis gas.

In certain preferred embodiments of the catalysts of the present invention, chromium-containing macroporous three-dimensional structures, or monoliths are provided which are self-supporting chromium-containing catalysts made of reticulated ceramic materials or three-dimensional ceramic foams.

Preferred methods of making the chromium oxide-containing catalysts include processing a chromium oxide powder in a reducing atmosphere to avoid production and evolution of volatile chromium compounds (e.g., CrO_3) during heating.

5 In some embodiments of the new catalysts, catalyst structures comprising a higher surface area active catalyst phase formed on top of a preformed reticulated ceramic foam are provided.

10 In other embodiments of the new catalysts, less active or non-catalytically active monoliths comprising reticulated ceramic materials, or three-dimensional ceramic foams, containing one or more metal oxides of chromium, aluminum, zirconium, titanium, magnesium, cobalt, nickel and silicon are provided. These structures serve as non-poisoning supports for active or more active catalyst materials for various oxidations, including methane oxidation to synthesis gas. Another aspect of the present invention is a process or method of making the above-described catalysts and support structures.

15 Yet another aspect of the invention comprises a process or method of converting a gaseous methane or other light hydrocarbon feedstock, together with an oxygen source and, optionally, nitrogen, catalyzed by one of the above-described catalysts, to yield a product containing a mixture of carbon monoxide and hydrogen gases. Still other embodiments and advantages of the present invention will appear from the following description.

BRIEF DESCRIPTION OF THE DRAWING

20 Fig. 1 is a graph showing the on-stream life over a test period of more than 24 hrs of a representative $\text{NiO}, \text{MnO}, \text{MgO}$ foam catalyst bed.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

25 Methods of making macroporous monolithic, self-supporting active catalyst structures and non-poisoning catalyst support structures having a high surface-area-to-volume ratio (preferably $0.1\text{-}250\text{ m}^2/\text{g}$ measured by N_2 BET) are described in the following examples. As explained in more detail below, the active catalytic monoliths or non-poisoning supports are formed by calcining a salt solution of chromium, cobalt, nickel, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium or phosphorus, forming a solution or slurry of the calcined material and impregnating an organic pore-templating material. The impregnating solution or slurry may also include metal oxides chosen from 30 the group consisting of an oxide of chromium, cobalt, nickel, alkaline earth, rare earth, or other sinterable metal oxide that is capable of catalyzing an oxidation reaction.

Porous catalysts containing chromium oxide as a major component, in particular, have not been described previously. The inventors have discovered that processing of Cr_2O_3

to make a chromium oxide reticulated foam requires a significant variation from conventional metal oxide foam forming methods. As some of the following comparative examples will show, processing in air will not form a self-sustaining structure. The new chromium oxide reticulated ceramic three-dimensional structures are processed in a reducing atmosphere to form a mechanically strong and catalytically useful structure. The new chromium-containing reticulated ceramic catalysts and non-poisoning supports, as well reticulated ceramic monoliths containing metal oxides other than chromium have been evaluated for their catalytic activity in syngas production processes.

A non-poisoning ceramic foam support may have a similar or identical composition to that of a higher surface area, active catalyst layer supported on it. In such case, the support is non-poisoning because, since it has the same composition as the active phase, no additional elements or phases are introduced into the catalyst layer as a consequence of interdiffusion at calcination temperatures, or at the temperatures of the syngas or other millisecond contact time reactions. This non-poisonous feature also makes these reticulated ceramic three-dimensional structures useful as active catalysts and catalyst supports for applications other than syngas production.

In the following examples, the metal components of the catalyst compositions are given in atomic ratios of the total metal content, unless otherwise indicated.

Example 1: Cr_2O_3 Foam (Comparative Example).

A Cr_2O_3 ceramic foam was prepared using a Cr_2O_3 powder which had been calcined in air. An aqueous solution of $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{CO}_2)_7$ (100 mL, 2.5603 M) was added to a 150 mL petri dish and rapidly frozen with liquid nitrogen. The frozen solid was dried under vacuum for several days (approximately 7 days) to produce a freeze dried powder. The freeze dried material was heated in air at 350°C for 5 hours and 525°C for 1 hour prior to use. The resulting powder was then formed into a 3-D monolith structure by impregnating a polyurethane foam with an aqueous slurry or solution containing the powder (i.e., the active catalyst precursor). A technique such as that described by Brown and Green (*J. Am. Ceram. Soc.* 1994. 77:1467-72) for the "polymer foam replication process" was used to prepare the slurry and to load the pore-templating material, such as polyurethane foam. During impregnation the foam pores were filled with slurry and any excess slurry was filtered off (similar to the foam loading technique described in example 6 of U.S. Pat. No. 4,810,685.) The slurry may also include a dispersant, binder or wetting agent to facilitate loading. The loaded polyurethane foam was dried at about 110-120°C and calcined at a low temperature

(i.e., about 800°C) in air to remove the polyurethane foam to yield a "green" reticulated ceramic. A final, higher temperature calcination (i.e., 1000-1600°C) was applied to sinter the material and impart mechanical strength. As a result of its being prepared by calcination in an oxidizing atmosphere, however, the resulting foam was friable, crumbled upon handling, and proved to be completely mechanically unstable.

A procedure identical to Example 1 was repeated, except that a temperature of 1,610°C, in air, was used to densify the material. The resulting material was also friable and crumbled upon handling.

Example 2: $\text{Co}_{0.2}\text{Cr}_{0.8}\text{Ox}$ Foam (Comparative Example).

A $\text{Co}_{0.2}\text{Cr}_{0.8}\text{Ox}$ ceramic foam was prepared using a $\text{Co}_{0.2}\text{Cr}_{0.8}\text{Ox}$ starting material powder, prepared as follows: $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Aldrich) 167.60 g was dissolved in water. To that solution, 900 ml of 2.5603 M solution of $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{COO})_7$ (Aldrich, 31810-8) was added. The final powder was heated at a rate of 5°C/min to 350°C, allowed to soak at 350°C for 5 hours, and then heated to 525°C (5°C/min), and allowed to soak at 525°C for one hour in air. The resulting powder was then formed into a monolith by impregnating a polyurethane foam, as described in Example 1. Similar to the Cr_2O_3 ceramic foam, this material was also completely unstable with respect to handling, as it was also friable and readily crumbled.

In a similar study, an identical procedure as described in the foregoing paragraph was employed, except that the powder was milled prior to impregnating it into the polyurethane foam. Powder was hand ground to a particle size, $d_{50} = 14.7$ micrometers in diameter (i.e., 50 volume % of the powder is < 14.7 micrometers in diameter), and ball milled in the aqueous slurry to approximately $d_{50} = 2.3$ micrometers, with 14 volume % < 1 micrometer. All particle size measurements in this and subsequent examples were performed using laser scattering on a Horiba LA900 Particle Size analyzer. The final foam material was heated at 1650°C, for 2 hours in air. Similar to the Cr_2O_3 ceramic foam, this material was also completely unstable with respect to handling, as it was also friable and readily crumbled.

In another study like that described above, the powder was ball milled for an additional 24 hours to produce a particle size of $d_{50} = 1.0$ micrometers, with 48 volume % below 1 micrometer in diameter. The final foam material was heated at 1650°C, for 2 hours in air. Similar to the Cr_2O_3 ceramic foam, this material was also completely unstable with respect to handling. It was friable and readily crumbled.

Example 3: 0.2% $\text{Ni}_{0.2}\text{Cr}_{0.8}$ /Cordierite Ceramic Foam (Comparative Example).

A $\text{Ni}_{0.2}\text{Cr}_{0.8}$ /Cordierite ceramic foam approximately 0.2 wt% (as the oxides of nickel and cobalt) was prepared as follows: 1.0120 g of a mixed solution containing 1:4 molar ratio, Ni:Cr (prepared by mixing 7.1043 ml of 0.033782 M $(\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{COO})_7$ (Aldrich, 31,810-8) with 0.0561 ml of 1.068 M $\text{Ni}(\text{NO}_3)_2$ molarity determined by ICP analysis)) was added to cordierite honeycomb, 600 cpi, 12mm OD x 10 mm H. The entire honeycomb was rapidly frozen in liquid nitrogen and evacuated for several days and calcined in air according to the following schedule: 5°C/min to 350°C, soak 350°C 5 hours, 5°C/min to 525°C, soak 525°C 1 hour, 10°C/min to room temperature.

10 Example 4: 2% $\text{Co}_{0.2}\text{Cr}_{0.8}$ in Cordierite Honeycomb (Comparative Example).

An approximately 2 wt % $\text{Co}_{0.2}\text{Cr}_{0.8}$ in Cordierite Honeycomb, 400cpi, 10mm x 12mm O.D. was prepared as follows: A mixed solution containing 2.9337 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa 11341) dissolved in 15.74 ml of 2.56 M aqueous chromium solution, prepared using $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{COO})_7$ (Aldrich, 31810-8). A cordierite honeycomb (400 cpi) was loaded with this solution, frozen with liquid nitrogen, and evacuated (freeze dried) for several days. The monolith was then calcined in air according to the following schedule: 5°C/min to 350°C, soak 350°C 5 hours, 5°C/min to 525°C, soak 525°C 1 hour, 10°C/min to room temperature. The weight of the oxides remaining on the monolith constituted about 2 wt % of the total weight.

20 Example 5: Cr_2O_3 Ceramic Foam

The identical Cr_2O_3 powder, as described in Example 1 was used. However, in contrast to the composition of Example 1, densification of the Cr_2O_3 was achieved in this Example by calcination of the foam in a non-oxidizing, inert or reducing atmosphere. An aqueous solution of $\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{CO}_2)_7$ (100 mL, 2.5603 M) was added to a 150 mL petri dish and rapidly frozen with liquid nitrogen. The frozen solid was dried under vacuum for several days (approximately 7 days) to produce a freeze dried powder. The freeze dried material was heated in air at 350°C for 5 hours and 525°C for 1 hour prior to use. The resulting powder was then formed into a 3-D monolith structure by impregnating a polyurethane foam with an aqueous slurry or solution containing the powder (i.e., the active catalyst precursor). A technique such as that described by Brown and Green (*J. Am. Ceram. Soc.* 1994. 77:1467-72) for the "polymer foam replication process" was used to prepare the slurry and to load the pore-templating material, such as polyurethane foam. During impregnation the foam pores were filled with slurry and any excess slurry was filtered off

(similar to the foam loading technique described in example 6 of U.S. Pat. No. 4,810,685, the disclosure of which is incorporated by reference.) The loaded polyurethane foam was dried at about 110-120°C and calcined at a low temperature (i.e., about 800°C) in air to remove the polyurethane foam to yield a "green" reticulated ceramic.

- 5 A final, higher temperature heating step in a covered crucible, filled with carbon powder to impart a reducing atmosphere, at 1500-1600°C for 2 hours was applied to sinter and densify the material and impart mechanical strength. The material, at this point, was not friable, and did not readily crumble upon handling. It possessed sufficient mechanical strength to be used in the millisecond contact time reactor. Processing in this manner to form
- 10 a Cr_2O_3 foam structure constitutes a significant departure from conventional methods of making ceramic foams. The pure Cr_2O_3 foam was tested (as a two-piece stack) in a reduced scale syngas production reactor, as described in the section entitled "Test Procedure." No light-off was observed for the Cr_2O_3 foam.

- The resulting reticulated ceramic foam demonstrated the required macroporosity to
- 15 minimize back pressure while having sufficient tortuosity, thermal heat resistance and mechanical strength for use at high volumetric flow rates. As shown in the following examples, this chromium oxide foam serves as an excellent, non-poisoning support for more active catalyst compositions. Some preparations of the pure chromium oxide reticulated ceramics possess N_2 BET surface areas less than $1 \text{ m}^2/\text{g}$ (i.e., the material is extremely
- 20 macro (but not micro or meso) porous.) The preferred catalyst particle surface area ranges from 0.1 to $250 \text{ m}^2/\text{g}$.

- Although a covered crucible filled with carbon powder to impart a reducing atmosphere during the higher temperature heating step is described in the present example, any method that prevents the oxidation of the chromium oxide foam during the high
- 25 temperature final densification step can be used to produce an acceptable reticulated ceramic structure. Such methods include heating in a reducing atmosphere such as flowing hydrogen, in a vacuum or in an inert atmosphere.

Example 6: $\text{Ni}_{0.2}\text{Cr}_{0.8}$ on Preformed $\text{Co}_{0.2}\text{Cr}_{0.8}$ Ox foam

- $\text{Ni}_{0.2}\text{Cr}_{0.8}$ (1:4, Ni: Cr molar ratio) powder supported on the cobalt/chromium oxide
- 30 reticulated ceramic foam from Example 18, below, was prepared. A 1:4 molar ratio solution of Ni:Cr (prepared by mixing 7.1043 ml of 0.033782M $(\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{COO})_7$ (Aldrich, 31,810-8) with 0.0561 ml of 1.068 M $\text{Ni}(\text{NO}_3)_2$ (molarity determined by ICP analysis)) was diluted by a factor of 10 (2 ml was diluted with water to 20 ml). 0.5366 g of this solution

was added to a 12 mm diameter x 10 mm H, 80 ppi $\text{Co}_{0.2}\text{Cr}_{0.8}\text{O}_x$ ceramic foam, whose preparation is described below in Example 18. The liquid-loaded foam was frozen with liquid nitrogen and evacuated for several days while frozen. The final material was calcined in air according to the following schedule: 5°C/min to 350°C, soak 350°C 5 hours, 5°C/min to 525°C, soak 525°C 1 hour, 10°C/min to room temperature. The foam was tested in a reduced scale syngas production reactor, as described in the section entitled "Test Procedure." The test results are shown in Table 1. This reticulated ceramic foam demonstrated sufficient macroporosity to minimize back pressure while having sufficient tortuosity, thermal heat resistance and mechanical strength for use at high volumetric flow rates.

Example 7: $\text{Ni}_{0.2}\text{Cr}_{0.8}$ on Cr_2O_3 Foam (Full Impregnation).

$\text{Ni}_{0.2}\text{Cr}_{0.8}$ on Cr_2O_3 foam using the Cr_2O_3 foam described in Example 5. 10 ml of 1.6575 M of chromium hydroxide acetate ($\text{Cr}_3(\text{OH})_2(\text{CH}_3\text{COO})_7$, (Aldrich, 31,810-8), was mixed with 3.88 ml of 1.068 M $\text{Ni}(\text{NO}_3)_2$ solution (molarity checked by ICP analysis). This solution was diluted by a factor of six, so that final molarity of Cr is 0.1990 M, and of Ni is 0.04976 M. At that point, 0.8789 g of a chromium oxide reticulated ceramic foam (80 ppi) was used. 0.5930 g of the solution was added to the ceramic foam, to fill the macropores (full impregnation). The liquid was allowed to evaporate, and the ceramic piece was then calcined according to the following schedule, in air: 5°C/min to 350°C, soak 350°C 5 hours, 5°C/min to 525°C, soak 525°C 1 hour, 10°C/min to room temperature. The final loading of metal oxides was approximately 1.26 wt % ($\text{Ni}_{0.2}\text{Cr}_{0.8}$ oxide, assuming Ni^{2+} and Co^{2+}). The foam was tested (as a two-piece stack) in a reduced scale syngas production reactor, as described in the section entitled "Test Procedure." The test results are shown in Table 1.

Example 8: $\text{Ni}_{0.2}\text{Cr}_{0.8}$ on Cr_2O_3 Foam (Cylindrically Impregnated).

$\text{Ni}_{0.2}\text{Cr}_{0.8}$ on Cr_2O_3 foam was prepared using the same solutions as described in the previous example, and a similar procedure. In this case, however, the outside of the cylindrical ceramic piece was wetted with the solution, but not the center. 0.2014 g of the solution was added to the monolith in this manner. Further processing (i.e., drying, calcination) was identical to that described in the previous example. The final loading of metal oxides is approximately 0.44 wt % ($\text{Ni}_{0.2}\text{Cr}_{0.8}$ oxide, assuming Ni^{2+} and Co^{2+}).

Cr-containing ceramic foams prepared according to the foregoing examples were tested as described in the section entitled "Test Procedure." The results obtained upon testing these composition in a reduced scale syngas production reactor are shown in Table 1.

Table 1

| Catalyst | Conditions | % CH ₄ Conv. | % O ₂ Conv. | % CO Sel | % H ₂ Sel | H ₂ :CO Ratio | % CO ₂ Sel | Run time (hr) |
|--|--|--|---------------------------|-------------|-------------------------|-----------------------------|--------------------------|------------------|
| (Example 4) | | | | | | | | |
| Co _{0.2} Cr _{0.8} /Honeycomb | Light-off, 290°C | Shortly after switch to methane the reactor crashed on over temp | | | | | | |
| 400cpi, 12mm O.D. x 10mm H | | | | | | | | |
| Prep. by freeze dry | | | | | | | | |
| (Example 18) | | | | | | | | |
| Cr/Co foam | light-off, 640°C | 46 | 100 | 78 | 62 | 1.60 | 22 | 2 |
| 12mm OD x 10mm H | 2.5 NLPM, 5psig Air feed 1117°C cat. | | | | | | | |
| (Example 6) | | | | | | | | |
| 0.1% Ni _{0.2} Cr _{0.8} /Cr foam | O ₂ feed light-off, 510°C | | | | | | | |
| 80ppi, used foam | 2.5 NLPM, 5psig | 70 | 100 | 93 | 88 | 1.9 | 7 | 3.5 |
| 12mm OD x 10mm H | 515°C PH | | | | | | | |
| Freeze dry prep | 1161°C catal | | | | | | | |
| (Example 3) | | | | | | | | |
| 0.2% Ni _{0.2} Cr _{0.8} /Cordierite | | propane light-off at 750°C, Did not stay ignited at CH ₄ switch | | | | | | |
| 600cpi honeycomb | | restart produced the same result. | | | | | | |
| 12mm OD x 10 mm H | Freeze dried | | | | | | | |
| (Example 1) | | | | | | | | |
| Cr ₂ O ₃ foam, 80ppi | | No light-off observed | | | | | | |
| 2 pieces, 10mm OD x 8 mm H each | | | | | | | | |
| (top) 0.44% (NiCrO _{1.5})/Cr ₂ O ₃ | O ₂ feed 2.5 NLPM | Light off occurred at 420°C, first attempt failed at CH ₄ switch. | | | | | | |
| (side impregnated) | 5 psig | | | | | | | |
| (bottom) 1.26% (Ni _{0.2} Cr _{0.8})/Cr ₂ O ₃ | 508°C PH | Very little conversion detected (trace amounts of CO ₂ , H ₂ , H ₂ O) | | | | | | |
| (full impregnation) | 782°C catal | | | | | | | |

Example 9 : 13% Ni/MgO Foam

- 5 A NiO-MgO foam (80 ppi) 10mm x 12 mm OD was prepared from the corresponding powder. Ni(NO₃)₂·6H₂O (19.325g) was dissolved in distilled water (50 mL) to give wet impregnation when mixed with calcined (600°C for 3 hours) MgO (26.1 g). The slurry was mixed with a spatula, and dried at 110°C, followed by calcining at 800°C for

2 hours. A portion of the calcined material (15 g) was reduced in flowing hydrogen (about 100 cc/minute) for 4 hours at 800°C. The resulting hydrogen-reduced material was sized to 20-30 mesh (0.84-0.59 mm average diameter) powder. The powder was made into an aqueous solution or slurry and then formed into a monolith by impregnating a polyurethane foam, as described in Example 1. The resulting monoliths were tested in a reduced scale syngas production reactor as described in the section entitled "Test Procedure." The results are shown in Table 2. In Table 2 the percent conversion of CH₄ and O₂ reactant gases, the product selectivity of CO and H₂, the ratio of the product gases and the operating conditions are given for both one piece (10mm) and two piece (20mm) beds of NiO-MgO foams.

Table 2

NiO-MgO Reticulated Ceramic Foam Fired at 1000°C

| <u>Catalyst</u> | <u>Temp</u> <u>(°C)</u> | <u>SLMP</u> | <u>%CH₄/O₂</u> <u>Conv.</u> | <u>%CO/H₂</u> <u>Sel.</u> | <u>H₂:CO</u> <u>Ratio</u> |
|----------------------------|----------------------------|-------------|--|---|---|
| NiO-MgO foam (10mm x 12mm) | 771 | 2.5 | 84/100 | 96/95 | 1.98 |
| 1 piece | 884 | 7.5 | 89/100 | 98/95 | 1.94 |
| NiO-MgO foam (10mm x 12mm) | 693 | 2.5 | 86/100 | 96/95 | 1.98 |
| 2 pieces | 836 | 7.5 | 91/100 | 98/97 | 1.98 |

Feed: 60%CH₄, 30%O₂, 10%N₂

Example 10: 3%Mn/13%Ni/MgO Reticulated Ceramic Foam

The preparation of the Mn(O)-Ni(O)/MgO powder catalyst was similar to that of Example 9 except that Mn(NO₃)₂·6H₂O (4.702 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2 g). The powder catalyst was then prepared by impregnating calcined MgO (Aldrich) with the aqueous solution of Ni nitrate and Mn nitrate followed by drying and calcining, as previously described.

The resulting powder was then formed into a 3-D monolith structure by impregnating a polyurethane foam with a slurry or solution containing the powder, as previously described in Examples 1 and 9, and fired at 1000°C. The final foam monolith, or bulk 3-dimensional form, contained about 80 pores per inch (ppi). The concentration of the nickel nitrate and manganese nitrate solution was such that the final NiO-MnO-MgO foam pieces (12mm OD x 10mm H) contained 13%Ni, 3%Mn/MgO powder catalyst. Table 3 gives the ICP (inductively coupled plasma) compositional analysis for elemental composition for this foam. Fig. 1 shows CH₄ conversion, CO/H₂ selectivity, and catalyst

temperature with run time (two 10 mm high monoliths were stacked to form a 20mm high bed). It can be seen that CH₄ conversion was constant at 90% and syngas selectivity was constant at 95+%. The bed temperature remained constant below 800°C for at least 25 hours run time. By contrast, under the same test conditions a honeycomb catalyst of Ni(O), Mn(O),Mg(O) on cordierite (Johnson Matthey EP-5170) consisting of two stacked pieces 12 mm OD x 10 mm H ran fairly consistently at 90% CH₄ conversion and more than 95% syngas selectivity to about 25 hrs run time. At that point, the bed temperature rose from 850°C to 1000°C over the next 10 hours, and the conversion and H₂ selectivity declined slightly. This deterioration appears to be attributable to the support effect of the cordierite.

(data not shown)

Table 3

| Element | Wt % |
|---------|---------|
| Ni | 11.2 |
| Mn | 2.83 |
| Mg | 47.1 |
| Ca | 0.74 |
| Si | 0.31 |
| Na | 0.18 |
| Ti | 815 ppm |
| Fe | 700 ppm |

Example 11: 3% Mo/13% Ni/MgO

The preparation of the monolithic catalyst powder was similar to that of Example 9 except that (NH₄)₂MoO₄ (1.8386 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2 g). The reticulated foam monolith was prepared as described in Example 9.

Example 12: 3% W/13% Ni/MgO

The preparation of the catalyst powder was similar to that of Example 9 except that (NH₄)₂WO₄ (1.3900 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2g). The reticulated foam monolith was prepared as described in Example 9.

Example 13: 3% Sn/13% Ni/MgO

The preparation of the catalyst powder was similar to that of Example 9 except that SnSO₄ (1.6281g) was also dissolved in the nickel solution before impregnation of the MgO (25.2g). The reticulated foam monolith was prepared as described in Example 9.

Example 14: 3% Re/13% Ni/MgO

The preparation of the catalyst powder was similar to that of Example 9 except that NH_4ReO_4 (1.2965 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2g). The reticulated foam monolith was prepared as described in Example 9.

5 **Example 15: 3% Bi/13% Ni/MgO**

The preparation of the catalyst powder was similar to that of Example 9 except that $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (2.089 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2g). The reticulated foam monolith was prepared as described in Example 9.

Example 16: 3% In/13% Ni/MgO10

The preparation of the catalyst powder was similar to that of Example 9 except that $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (3.0641 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2g). The reticulated foam monolith was prepared as described in Example 9.

Example 17: 3% P/13% Ni/MgO15

The preparation of the catalyst powder was similar to that of Example 9 except that $\text{NH}_4\text{H}_2\text{PO}_4$ (3.3424 g) was also dissolved in the nickel solution before impregnation of the MgO (25.2g). The reticulated foam monolith was prepared as described in Example 9.

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The ceramic foam compositions containing various promoter metals, Ni and MgO, prepared as described in Examples 11-17, are expected to provide similar syngas selectivity and CH_4 conversion levels to that of the 3%Mn/13% Ni/MgO reticulated ceramic foam of Example 10, as the corresponding powder catalysts (data not shown) demonstrated similar activities to that of the Mn(O)-Ni(O)/MgO powder catalyst which was employed in making the foam catalyst of Example 10.

Example 18: Co-Cr Oxide Reticulated Foam25

Co-Cr oxide foam was prepared using $\text{Co}_{0.2}\text{Cr}_{0.8}\text{Ox}$ powder catalyst like that described in Example 2. The powder $\text{Co}_{0.2}\text{Cr}_{0.8}\text{Ox}$ catalyst was prepared by freezing an aqueous solution of the corresponding metal salts with liquid nitrogen, drying the frozen solution in a freeze drier, and calcining, as described in Example 2. The reticulated foam monolith was prepared as described in Example 2, except in the case of this chromium oxide system, a reducing atmosphere was maintained during the densification or sintering step in order to prevent the formation of volatile CrO_3 , as described for Example 5. The powder was ball milled to a particle size range (d50 of about 2 micrometers). The final material was densified by heat at 1600°C , for 2 hours, in a covered crucible containing carbon powder to

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provide a reducing/non-oxidizing atmosphere. Table 4 shows the extent of CH₄ and O₂ conversion and product CO and H₂ selectivities for this Co-Cr foam.

Example 19: 15% (Ni, Mn/MgO)/NiMgO Washcoated Reticulated Foam

A NiO-MgO foam fired at 1600°C was washcoated with 13% Ni, 3% Mn/MgO powder. In washcoating, the powder catalyst was first ground to less than 325 mesh and sufficient water was added to form a slurry. The preformed NiO-MgO foam was then dipped into the slurry and saturated for 5 minutes. The foam was removed from the slurry and dried at about 110°C for 2 hrs, but not calcined. The elemental composition of this foam was similar to that given in Example 10. Test results are shown in Table 4.

When a representative Ni(O)-Mn(O)-MgO reticulated ceramic monolith (fired at 1000°C) was tested (two pieces each 12 mm OD x 10 mm H), performance and catalyst run temperature were steady over the 24 hr period, as shown in Fig. 1. The system pressure was approximately 8 psig. The bed temperature was approximately 820°C. Results were steady at approximately 90% CH₄ conversion, 98% CO selectivity and 97% H₂ selectivity. These data show that the active catalyst composition can serve as the reticulated foam support. Samples of NiO-MnO-MgO reticulated foam made at 1600°C (the second, higher temperature calcination) were tested after being calcined, and very little conversion to CO and H₂ was detected in each case. The foam made at 1200°C also gave little conversion when tested.

Example 20: 6%(Ni, Cr)/NiMgO Washcoated Reticulated Foam

A NiO-MgO foam fired at 1600°C was washcoated with 6 wt% Ni_{0.2}Cr_{0.8} Ox freeze dried powder, prepared as previously described in a reducing atmosphere. In washcoating, the powder catalyst was first ground to less than 325 mesh and sufficient water was added to form a slurry. The preformed NiO-MgO foam was then dipped into the slurry and saturated for 5 minutes. The foam was removed from the slurry and dried at about 110°C for 2 hrs, but not calcined. Test results are shown in Table 4.

Example 21: Ni,Cr/Co-Cr Oxide Washcoated Reticulated Foam

The Co-Cr oxide reticulated foam was prepared as described in Example 18. The foam was coated with Ni_{0.2}Cr_{0.8}Ox by the wash coating technique described in Example 20. The foam was sintered or densified in a reducing atmosphere, as described in Example 18. After coating with the Ni_{0.2} Cr_{0.8} oxide precursor, it was heated at low temperatures to decompose the precursors on the pre-formed foam. Test results are shown in Table 4.

Test Procedure

Representative catalysts prepared as described in the foregoing Examples were tested in a reduced scale millisecond contact time reactor for their ability to convert a reactant gas mixture of CH₄, O₂, N₂ to synthesis gas. A 25 cm long quartz tube reactor was equipped with a co-axial, quartz thermocouple well, resulting in a 12.5 mm i.d. reactor. The void space within the reactor was packed with quartz chips. The catalyst bed, of compatible diameter (i.e., 12 mm OD), was positioned with quartz wool at approximately mid-length in the reactor. The foam monoliths were generally 8-10 mm in length, although in some cases two such pieces were stacked to provide a total catalyst bed length of 20 mm. A three point, K type, thermocouple was used with the catalyst's "hot spot", read-out temperature reported as the run temperature. The catalyst bed was heated with a 4 inch (10.2 cm), 600 W band furnace at 90% electrical output. Mass flow controllers and meters regulated the feed composition and flow rate. Prior to start-up, the flows were checked manually with a bubble meter and then the feed composition was reconfirmed by gas chromatographic analysis. The flow rates of all the meters were safety interlocked and their measurements were checked electronically by the mass flow meters every second. All runs were performed at a CH₄:O₂ feed ratio of 2:1, safely outside of the flammable region. The feed contained (in volume percent) 30% CH₄, 15% O₂ and 55% N₂ or 60% CH₄, 30% O₂ and 10% N₂. Experiments were conducted at 5 psig (136 kPa) or more, and a total flow rate of up to about 7.5 SLPM. The reactor effluent was analyzed by a gas chromatograph (g.c.) equipped with a thermal conductivity detector. The feed components (i.e., CH₄, O₂, N₂) and potential products (i.e., CO, H₂, CO₂, and H₂O) were all well resolved and reliably quantified by two chromatography columns in series consisting of 5A molecular sieve and Haysep T. Mass balances of C, H, and O all closed at 98-102%. Runs were conducted over two operating days, each with 6 hours of steady state, run time. The results of tests obtained with the representative 3-D catalyst structures in the reduced scale reactor runs are indicative of their applicability, when increased to industrial-scale dimensions, for commercial syngas production processes.

GHSV is gas hourly space velocity, i.e., liters of gas (measured at atmospheric pressure and 23°C) fed per hour per liter of catalyst. The GHSV is generally calculated as follows:

$$\text{GHSV} = F_{\text{tot}}/V_{\text{cat}}$$

where F_{tot} is the total reactant volumetric flowrate at standard conditions in cm³/sec, and V_{cat} is the volume of the catalyst reaction zone in cm³. For example, the volume of the catalyst

reaction zone is simply the volume of the cylinder (e.g., 12 mm in diameter x 10 mm in length, or 1.2 cm³). Thus, at a flowrate of 7.5 standard liters per minute (SLPM) (7,500 cm³/min), the GHSV is calculated as follows:

$$\text{GHSV (hr}^{-1}\text{)} = (7,500 \text{ cm}^3/\text{min}) / (1.2 \text{ cm}^3) \times (60 \text{ min/hr}) = 549,000 \text{ hr}^{-1}.$$

- 5 At GHSVs of 100,000 hr⁻¹ or more the residence or contact time of the reactant gas mixture on the catalyst is very short (i.e., preferably less than about 10 milliseconds).

Expressed in terms of volume of gas per weight of catalyst (NL/kg/hr.), for monolith supported catalysts having densities ranging from about 0.5 kg/l to about 2.0 kg/l, a GHSV of about 10,000 to 200,000,000 hr⁻¹ corresponds to about 20,000 to 100,000,000
10 normal liters of gas per kilogram of catalyst per hour (NL/kg/h).

From the results of testing the above-described compositions, it was determined by the inventors that the new reticulated ceramic monoliths have sufficient macroporosity to minimize back pressure when used on-stream, and possess better tortuosity and thermal heat resistance characteristics than conventional oxidation catalysts. These new structures
15 also possess good mechanical strength for use at high volumetric flow rates on stream in such applications as reduced scale, high flow rate syngas production reactors, for extended periods of time. The comparative performance of representative reticulated foams, which were prepared according to some of the foregoing examples, are shown in Table 4. For the chromium oxide based foam materials, using a Co_{0.2} Cr_{0.8} oxide reticulated ceramic as
20 a base material (Example 6 in Table 1, and the first entry in Table 4) appears to be superior to using the pure Cr₂O₃ foam base (last two entries in Table 1) when Ni_{0.2} Cr_{0.8} oxides are supported on it. In Table 4, the Ni_{0.2} Cr_{0.8} Ox/ Co_{0.2} Cr_{0.8} Ox foam is superior in performance to the performance of the pure Co_{0.2} Cr_{0.8} Ox foam (comparing the first and second rows of Table 4). Importantly, the sample prepared according to comparative
25 Example 4 (Co_{0.2} Cr_{0.8} on cordierite honeycomb; Table 1 and Table 5) shows that not all 3-D supports are useful. In that case no activity was observed, as the system crashed on overtemp.

Table 4

Performance of Reticulated Foams^a

| 30 | <u>Catalyst</u> | <u>Temp</u> (°C) | <u>SLPM</u> | <u>%CH₂/O₂</u> <u>Conv.</u> | <u>%CO/H₂</u> <u>Sel.</u> | <u>H₂:CO</u> <u>Ratio</u> |
|----|--|---------------------|-------------|--|---|---|
| | Co-Cr foam ^b | 1117 | 2.5 | 46/100 | 78/62 | 1.60 |
| 35 | 0.1 % Ni _{0.2} Cr _{0.8} /Co-Cr foam ^d | 1161 | 2.5 | 70/100 | 93/88 | 1.89 |

Mn/Ni/MgO foam^c

| | | | | | | |
|----|--|------|-----|--------|-------|------|
| 5 | 15% (Ni,Mn,MgO)/NiMgO foam ^d | 791 | 2.5 | 84/100 | 96/95 | 1.98 |
| | | 875 | 5.0 | 89/100 | 98/97 | 1.98 |
| | | 910 | 7.5 | 87/99 | 98/95 | 1.94 |
| 10 | 6% Ni _{0.2} Cr _{0.8} NiMgO foam ^d | 814 | 2.5 | 84/100 | 96/95 | 1.98 |
| | | 926 | 5.0 | 88/100 | 97/95 | 1.96 |
| | | 1011 | 7.5 | 88/100 | 97/96 | 1.98 |

^a Feed: 60%CH₄, 30%O₂, 10%N₂^b Feed: 30%CH₄, 15%O₂, 55%N₂^c Only trace products detected^d Washcoated foam

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The Co_{0.2}Cr_{0.8} freeze-dried oxide as a reticulated foam gave 46% CH₄ conversion with 78% CO and 62% H₂ selectivities. The addition of a 0.1 wt% loading of Ni_{0.2}Cr_{0.8}Ox onto a reticulated foam comprised of Co_{0.2}Cr_{0.8} freeze-dried oxide improved the results to 70% CH₄ conversion, 93% CO selectivity and 88% H₂ selectivity. The Ni(O), Mn(O), MgO material as a reticulated foam, gave CH₄ conversions approaching 90% and syngas selectivities in the upper 90s (as shown in Fig. 1). Results improved significantly on adding a 15 wt% wash coating of Ni(O), Mn(O), MgO onto the corresponding NiMgO reticulated foam (fired at 1600°C), as shown in Table 4, compared to a bare NiO-MnO-MgO foam made at 1600°C, which gave very little conversion to CO and H₂ (see the discussion in Example 19). The wash coating of 6 wt% Ni_{0.2}Cr_{0.8} onto the reticulated foam of Ni(O) MgO (fired at 1600°C) gave up to 88% CH₄ conversion, 97% CO selectivity, and 96% H₂ selectivity. In general, as the total flow increased from 2.5 to 7.5 SLPM, the temperature increased along with performance.

The NiO-MnO-MgO foams fired at 1600°C, while themselves serving as poor catalysts for converting CH₄ to CO and H₂, proved to be very good supports for the wash coated active catalyst materials, thereby yielding very active supported catalysts. These higher temperature treated ceramic foams are expected to tolerate higher on-stream temperatures and pressures than the corresponding NiO-MnO-MgO foams sintered at lower temperatures (e.g., 1000°C and below), as well as many other conventional three-dimensional catalyst compositions.

The most preferred reticulated ceramic structures, prepared by impregnating organic polymer foams as described above, and/or by loading such non-poisoning reticulated supports with catalytically active material demonstrated superior conversion

levels and selectivities (for syngas products) when compared to catalysts loaded on various commercially-available supports, as shown in Table 5.

Table 5
Comparative Performance of Other 3-D Catalysts^a

| <u>Catalyst</u> | <u>Temp</u> <u>(°C)</u> | <u>SLPM</u> | <u>%CH₄/O₂</u> <u>Conv.</u> | <u>%CO/H₂</u> <u>Sel.</u> | <u>H₂:CO</u> <u>Ratio</u> |
|--|----------------------------|-------------|--|---|---|
| 6.5% Ni _{0.2} Cr _{0.8} Ox/honeycomb | 1178 | 2.5 | 51/87 | 90/84 | 1.87 |
| 9% Co _{0.2} Cr _{0.8} Ox/honeycomb ^b | | | | | |
| 12% Co _{0.2} Cr _{0.8} Ox/PSZ | 800 | 2.5 | 83/100 | 96/96 | 2.00 |
| 9% MgCo ₂ O ₄ /PSZ | 913 | 2.5 | 80/100 | 96/92 | 1.92 |
| 12% CoAl ₂ O ₄ /PSZ | 814 | 2.5 | 82/99 | 96/93 | 1.94 |
| 13% (Ni,Mn,MgO)/PSZ | 917 | 2.5 | 83/100 | 97/95 | 1.96 |
| 14% (Ni,Mn,MgO)/honeycomb ^c | 806 | 2.5 | 83/100 | 96/94 | 1.96 |
| | 973 | 5.0 | 84/99 | 97/92 | 1.90 |
| Ni ExMet Gauze | 1065 | 2.5 | 78/100 | 95/71 | 1.92 |

PSZ = partially stabilized zirconia

^a Feed: 60% CH₄, 30% O₂, 10% N₂

^b System crashed on overtemp.

^c Honeycomb coated with 4% MgO

To achieve better thermal balance and to prevent uncontrolled exotherms, mixed catalytic beds containing two or more reticulated ceramic monoliths (of different catalyst concentration or composition), prepared as described in the Examples, may be employed to obtain longer, graded composition catalyst beds. In arranging the monoliths which constitute the catalyst bed, a monolithic composition leading to a more exothermic process (e.g., CO₂ and H₂O formation) is placed nearest the reactant gas entry point, and is followed by a monolith containing an endothermic reforming catalyst. For example, more strongly oxidizing, catalytic three-dimensional forms are positioned on top of the bed, followed by three-dimensional forms that catalyze reforming.

Although the preferred method of preparing the metal oxide powders for use in making the new reticulated foam catalysts includes freeze drying the metal salt solutions, satisfactory catalyst powders may also be made by any of various other techniques that have been customarily used to prepare catalyst powders and have been described in the

literature. For example, xerogel or aerogel formation, spray drying or spray roasting techniques. In any case, however, it is important that when the monolith-forming material includes chromium oxide, reducing conditions are required for the densification or sintering steps of preparing the ceramic foam. Preferably the reticulated foam catalysts have about 65-80 pores per inch.

The new reticulated ceramics, as exemplified above, in the form of three-dimensional monoliths have sufficient macroporosity to minimize back pressure when used on-stream, and possess better tortuosity and thermal heat resistance characteristics than conventional oxidation catalysts with non-3-dimensional forms. The new structures also possess good mechanical strength for use at high volumetric flow rates on stream in such applications as reduced scale, high space velocity syngas production reactors.

Process of Producing Syngas

A feed stream comprising a light hydrocarbon feedstock, such as methane, and an oxygen-containing gas is contacted with a reticulated foam catalyst prepared as described in one of the foregoing Examples. Alternatively, an active catalyst material supported by a non-poisoning reticulated foam, prepared as described in one of the foregoing examples, is used. Preferably a millisecond contact time reactor is employed, equipped for either axial or radial flow of reactant and product gases. Several schemes for carrying out catalytic partial oxidation (CPOX) of hydrocarbons in a short contact time reactor have been described in the literature. For example, L.D. Schmidt and his colleagues at the University of Minnesota describe a millisecond contact time reactor in U.S. Pat. No. 5,648,582 and in *J. Catalysis* 138, 267-282 (1992) for use in the production of synthesis gas by direct oxidation of methane over a catalyst such as platinum or rhodium. A general description of major considerations involved in operating a reactor using millisecond contact times is given in U.S. Patent No. 5,654,491. The disclosures of the above-mentioned references are incorporated herein by reference.

The hydrocarbon feedstock may be any gaseous hydrocarbon having a low boiling point, such as methane, natural gas, associated gas, or other sources of light hydrocarbons having from 1 to 5 carbon atoms. The hydrocarbon feedstock may be a gas arising from naturally occurring reserves of methane which contain carbon dioxide. Preferably, the feed comprises at least 50% by volume methane, more preferably at least 75% by volume, and most preferably at least 80% by volume methane.

The hydrocarbon feedstock is in the gaseous phase when contacting the catalyst. The hydrocarbon feedstock is contacted with the catalyst as a mixture with an oxygen-containing gas, preferably pure oxygen. The oxygen-containing gas may also comprise steam and/or CO₂ in addition to oxygen. Alternatively, the hydrocarbon feedstock is contacted with the catalyst as a mixture with a gas comprising steam and/or CO₂. It is preferred that the methane-containing feed and the oxygen-containing gas are mixed in such amounts to give a carbon (i.e., carbon in methane) to oxygen (i.e., oxygen) ratio from about 1.25:1 to about 3.3:1, more preferably, from about 1.3:1 to about 2.2:1, and most preferably from about 1.5:1 to about 2.2:1, especially the stoichiometric ratio of 2:1. The process is operated at atmospheric or superatmospheric pressures, the latter being preferred. The pressures may be from about 100 kPa to about 12,500 kPa, preferably from about 130 kPa to about 10,000 kPa. The process is preferably operated at temperatures of from about 600°C to about 1200°C, preferably from about 700°C to about 1100°C. The hydrocarbon feedstock and the oxygen-containing gas are preferably pre-heated before contact with the catalyst. The hydrocarbon feedstock and the oxygen-containing gas are passed over the catalyst at any of a variety of space velocities. Gas hourly space velocities (GHSV) for the process, stated as normal liters of gas per kilogram of catalyst per hour, are from about 20,000 to about 100,000,000 NL/kg/h, preferably from about 50,000 to about 50,000,000 NL/kg/h. Preferably the catalyst is employed in a millisecond contact time reactor for syngas production. The process preferably includes maintaining a catalyst residence time of no more than 10 milliseconds for the reactant gas mixture. Residence time is the inverse of the space velocity, and high space velocity equates to low residence time on the catalyst. The product gas mixture emerging from the reactor is harvested and may be sampled for analysis of products, including CH₄, O₂, CO, H₂ and CO₂. And, if desired, may be routed directly into a variety of applications. One such application is for producing higher molecular weight hydrocarbon components using Fisher-Tropsch technology.

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. For example, pure methane was employed in the representative test procedures, however, any light hydrocarbon (i.e., C₁-C₅) gaseous feedstock could also serve as a feedstock for the net partial oxidation reaction catalyzed by the new reticulated foam catalysts. Also, the reticulated ceramic materials described herein

may also have activity in various chemical oxidations other than methane oxidation to synthesis gas.

Any variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. For example, the foam structure described by the
5 inventors is only one of the workable monolithic configurations which the reticulated catalysts and non-poisoning supports may assume, and which will provide the requisite porosity and mechanical strength to the bed. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. The disclosures of U.S.
10 Provisional Application No. 60/183,576 and all patents and publications cited herein are incorporated by reference.

CLAIMS

What is claimed is:

1. A method of making a reticulated ceramic catalyst comprising:
 - drying an aqueous solution of at least one metal salt chosen from the group consisting of salts of chromium, cobalt, nickel, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium and phosphorus to yield a dried active catalyst or catalyst precursor material;
 - calcining said active catalyst or catalyst precursor material to yield a calcined catalyst or catalyst precursor material;
 - sizing said calcined material to yield an active catalyst or catalyst precursor powder comprising particles of predetermined average size;
 - preparing a solution or slurry containing said powder;
 - impregnating a pore-templating material with said solution or slurry;
 - drying said impregnated pore-templating material;
 - calcining said dry impregnated material at a first temperature to produce a green reticulated ceramic;
 - calcining said green reticulated ceramic at a second temperature higher than said first temperature sufficient to produce sintering of said ceramic, such that a catalytically active reticulated ceramic monolith is produced.
2. The method of claim 1 wherein said solution or slurry comprises at least one sinterable metal oxide capable of catalyzing an oxidation reaction.
3. The method of claim 1 wherein said at least one sinterable metal oxide is chosen from the group consisting of oxides of chromium, cobalt, nickel, alkaline earth elements and rare earth elements.
4. The method of claim 1 further comprising maintaining said ceramic in a non-oxidizing atmosphere during said higher temperature calcining,
5. The method of claim 1 wherein said impregnated material comprises a chromium salt and/or chromium oxide and said second calcining step comprises maintaining said ceramic in a non-oxidizing atmosphere during said calcining, said non-oxidizing atmosphere chosen from the group consisting of a vacuum, a hydrogen gas atmosphere, an inert gas atmosphere, and an atmosphere comprising a combination of hydrogen and at least one inert gas.

6. The method of claim 1 wherein said step of impregnating a pore-templating material with said powder-metal oxide solution or slurry comprises impregnating an organic polymer foam substrate.
7. The method of claim 1 wherein said step of calcining said dry impregnated material to yield a ceramic foam precursor is conducted at a temperature of no more than about 1000°C.
8. The method of claim 1 wherein said step of calcining said ceramic at a second temperature sufficient to produce sintering comprises heating to a temperature of about 1500-1600°C.
9. The method of claim 1 wherein said step of preparing a solution or slurry comprises including at least one additional component chosen from the group consisting of a dispersant, a binder, and a wetting agent.
10. The method of claim 1 wherein when said step of preparing a solution or slurry comprises including a chromium-containing compound, and said method further comprises maintaining said ceramic in a non-oxidizing atmosphere during said higher temperature calcining step.
11. The method of claim 1 wherein said step of sizing said calcined material comprises reducing said active catalyst or catalyst precursor material to particles less than about 325 mesh.
12. The method of claim 11 wherein said step of sizing said calcined material comprises reducing said active catalyst or catalyst precursor material to about 20-30 mesh particles.
13. A reticulated ceramic foam catalyst comprising the product of the process of claim 1.
14. A reticulated ceramic foam catalyst active for catalyzing the oxidation of methane to synthesis gas by a net partial oxidation reaction, said catalyst comprising chromium oxide, said reticulated ceramic foam catalyst having sufficient mechanical strength to withstand gas pressure up to about 12,500 kPa and temperatures up to about 1200°C, and having sufficient macroporosity to permit a space velocity of reactant and product gases up to at least about 100,000,000 NL/kg/h when employed on-stream in a short contact time reactor for synthesis gas production.
15. The reticulated ceramic foam catalyst of claim 14 containing about 65-80 pores per inch.

16. The reticulated ceramic foam catalyst of claim 14 having a surface area of about 5-250 m²/g.
17. The reticulated ceramic foam catalyst of claim 14 further comprising at least one sinterable metal or metal oxide chosen from the group consisting of chromium, cobalt, nickel, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium and phosphorus, alkaline earth metals and rare earth metals, and oxides thereof.
18. The catalyst of claim 17 comprising nickel oxide.
19. The catalyst of claim 17 comprising manganese oxide.
20. The catalyst of claim 17 comprising magnesium oxide.
21. The catalyst of claim 17 comprising cobalt oxide.
22. The catalyst of claim 17 comprising nickel oxide, manganese oxide, and magnesium oxide.
23. The catalyst of claim 17 comprising nickel oxide and cobalt oxide.
24. A reticulated ceramic catalyst support having sufficient mechanical strength and thermal heat resistance to withstand gas pressure up to about 12,500 kPa and temperatures up to at least about 1200°C, and sufficient macroporosity to permit a space velocity of reactant and product gases up to about 100,000,000 NL/kg/h when employed on-stream in a short contact time reactor for synthesis gas production, said support prepared by:
 - calcining a chromium-containing powder;
 - sizing said calcined powder to yield a chromium-containing powder comprising particles of less than 350 mesh;
 - preparing an aqueous solution or slurry containing said sized powder;
 - impregnating a pore-templating material with said solution or slurry;
 - drying said impregnated pore-templating material; and
 - sintering said impregnated material at about 1500-1600°C in a non-oxidizing atmosphere.
25. The catalyst support of claim 24 wherein said step of preparing an aqueous solution or slurry containing said sized powder further comprises including at least one additional component chosen from the group consisting of a dispersant, a binder and a wetting agent in said solution or slurry.
26. A reticulated ceramic catalyst support having sufficient mechanical strength and thermal heat resistance to withstand gas pressure up to about 12,500 kPa and

temperatures up to about 1200°C, and sufficient macroporosity to permit a flow rate of reactant and product gases up to about 100,000,000 NL/kg/h when employed on-stream in a short contact time reactor for synthesis gas production, said support prepared by:

- 5 preparing an aqueous slurry comprising magnesium oxide powder;
 impregnating a pore-templating material with said slurry;
 drying said impregnated pore-templating material; and
 sintering said impregnated material at about 1500-1600°C.
27. The catalyst support of claim 26 wherein said step of preparing an aqueous solution
10 or slurry comprising magnesium oxide powder further comprises including in said
 solution or slurry at least one sinterable metal or metal oxide capable of catalyzing
 an oxidation reaction.
28. The catalyst support of claim 27 wherein said at least one sinterable metal or metal
 oxide comprises a metal or metal oxide chosen from the group consisting of
15 chromium, nickel, manganese, molybdenum, tungsten, tin, rhenium, bismuth,
 indium, phosphorus, and oxides thereof.
29. A supported catalyst comprising an active catalyst component disposed on a non-
 poisoning reticulated ceramic support, said active catalyst component comprising a
 metal or metal oxide selected from the group consisting of chromium, cobalt, nickel,
20 manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium, phosphorus,
 alkaline earth metals, rare earth metals, and oxides thereof, said support structure
 comprising chromium oxide or magnesium oxide, and said support having sufficient
 mechanical strength and thermal heat resistance to withstand gas pressure up to
 about 12,500 kPa and temperatures up to about 1200°C, and sufficient
25 macroporosity to permit a flow rate of reactant and product gases up to about
 100,000,000 NL/kg/h when employed on-stream in a short contact time reactor for
 synthesis gas production.
30. The supported catalyst of claim 28 further including at least one other metal or metal
 oxide selected from the group consisting of chromium, cobalt, nickel, manganese,
30 molybdenum, tungsten, tin, rhenium; bismuth, indium, phosphorus, alkaline earth
 metals, rare earth metals, and oxides thereof.

31. The supported catalyst of claim 30 wherein said active catalyst component comprises 0.1 wt% $\text{Ni}_x\text{Cr}_y\text{O}_x$ and said support comprises a chromium oxide foam, wherein the subscript x is an atomic ratio of 0.2 and the subscript y is an atomic ratio of 0.8.
- 5 32. The supported catalyst of claim 30 wherein said support comprises cobalt oxide and chromium oxide foam.
33. The supported catalyst of claim 29 wherein said active catalyst component comprises 15 wt% of a composition containing 13wt% Ni (O), 3wt % Mn(O), 84wt% Mg(O), and said support comprises NiO-MgO foam.
- 10 34. The supported catalyst of claim 29 wherein said active catalyst component comprises 6 wt% $\text{Ni}_x\text{Cr}_y\text{O}_x$ and said support comprises NiO-MgO foam, wherein the subscript x is an atomic ratio of 0.2 and the subscript y is an atomic ratio of 0.8.
35. A method of converting a $\text{C}_1\text{-C}_5$ hydrocarbon to a product gas mixture containing CO and H_2 , the process comprising
- 15 mixing a $\text{C}_1\text{-C}_5$ hydrocarbon-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture;
- contacting said reactant gas mixture with a catalytically effective amount of a catalyst comprising at least one macroporous reticulated ceramic monolith containing chromium oxide; and
- 20 maintaining catalytic partial oxidation reaction promoting conditions.
36. The method of claim 35 wherein said step of maintaining catalytic partial oxidation reaction promoting conditions comprises, during said contacting, maintaining said catalyst structure and said reactant gas mixture at a temperature of about 600-1,100°C.
- 25 37. The method of claim 35 wherein said step of maintaining catalytic partial oxidation reaction promoting conditions comprises, during said contacting, maintaining said catalyst structure and said reactant gas mixture at a pressure of about 100-12,500 kPa.
- 30 38. The method of claim 35 wherein said step of maintaining catalytic partial oxidation reaction promoting conditions comprises passing said reactant gas mixture over said composition at a continuous space velocity of at least about 20,000 to about 100,000,000 NL/kg/h.

39. The method of claim 38 wherein said step of passing said reactant gas mixture over said catalyst comprises passing said mixture at a gas hourly space velocity of about 50,000 to about 50,000,000 NL/kg/h.
40. The method of claim 35 wherein said step of maintaining catalytic partial oxidation reaction promoting conditions comprises maintaining a contact time of less than about 10 milliseconds between said reactant gas mixture and said catalyst.
41. The method of claim 35 wherein said reticulated ceramic monolith further comprises at least one catalytically active metal or metal oxide chosen from the group consisting of cobalt, nickel, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium and phosphorus, and oxides thereof.
42. The method of claim 35 wherein said catalyst further comprises least one metal or metal oxide capable of catalyzing an oxidation reaction chosen from the group consisting of chromium, cobalt, nickel, alkaline earth metals, rare earth metals, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium and phosphorus, and oxides thereof, supported on said reticulated ceramic monolith.
43. The method of claim 35 wherein said mixing comprises mixing a methane-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1.
44. The method of claim 35 wherein said oxygen-containing feedstock further comprises steam, CO₂, or a combination thereof.
45. The method of claim 35 wherein said mixing comprises mixing a hydrocarbon feedstock and a gas comprising steam and/or CO₂ to provide said reactant gas mixture.
46. The method of claim 35 wherein said C₁-C₅ hydrocarbon comprises at least about 50 % methane by volume.
47. The method of claim 35 wherein said C₁-C₅ hydrocarbon comprises at least about 80 % methane by volume.
48. The method of claim 35 further comprising preheating said reactant gas mixture.
49. A method of converting a C₁-C₅ hydrocarbon to a product gas mixture containing CO and H₂, the process comprising
- mixing a C₁-C₅ hydrocarbon-containing feedstock and an oxygen-containing feedstock to provide a reactant gas mixture feedstock;
- contacting said reactant gas mixture feedstock with a catalytically effective amount of a catalyst comprising at least one macroporous reticulated ceramic

monolith containing magnesium oxide and a catalytically active material disposed on said ceramic monolith;

during said contacting, maintaining said catalyst structure and said reactant gas mixture at a temperature of about 600-1,100°C;

5 during said contacting, maintaining said catalyst structure and said reactant gas mixture at a pressure of about 100-12,500 kPa; and

passing said reactant gas mixture over said composition at a continuous flow rate of about 20,000 to about 100,000,000 NL/kg/h.

50. The method of claim 49 wherein said reticulated ceramic monolith further includes
10 at least one sinterable metal or metal oxide capable of oxidizing an oxidation reaction and chosen from the group consisting of chromium, cobalt, nickel, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium and phosphorus, and oxides thereof.

51. The method of claim 49 wherein said catalyst further includes at least one metal or
15 metal oxide capable of catalyzing an oxidation reaction chosen from the group consisting of chromium, cobalt, nickel, alkaline earth metals, rare earth metals, manganese, molybdenum, tungsten, tin, rhenium, bismuth, indium and phosphorus, and oxides thereof.

52. The method of claim 49 further comprising mixing a methane-containing feedstock
20 and an oxygen-containing feedstock to provide a reactant gas mixture feedstock having a carbon:oxygen ratio of about 1.25:1 to about 3.3:1.

53. The method of claim 49 wherein said oxygen-containing feedstock further comprises steam, CO₂, or a combination thereof.

54. The method of claim 49 further comprising mixing a hydrocarbon feedstock and a
25 gas comprising steam and/or CO₂ to provide said reactant gas mixture.

55. The method of claim 49 wherein said C₁-C₅ hydrocarbon comprises at least about 50 % methane by volume.

56. The method of claim 49 wherein said C₁-C₅ hydrocarbon comprises at least about 80 % methane by volume.

30 57. The method of claim 49 further comprising preheating said reactant gas mixture.

58. The method of claim 49 further comprising passing said reactant gas mixture over said catalyst at a gas hourly space velocity of at least about 20,000 - 100,000,000 normal liters of gas per kilogram of catalyst per hour (NL/kg/h).

59. The method of claim 49 wherein said step of passing said reactant gas mixture over said catalyst comprises passing said mixture at a gas hourly space velocity of at least about 50,000 to about 50,000,000 NL/kg/h.

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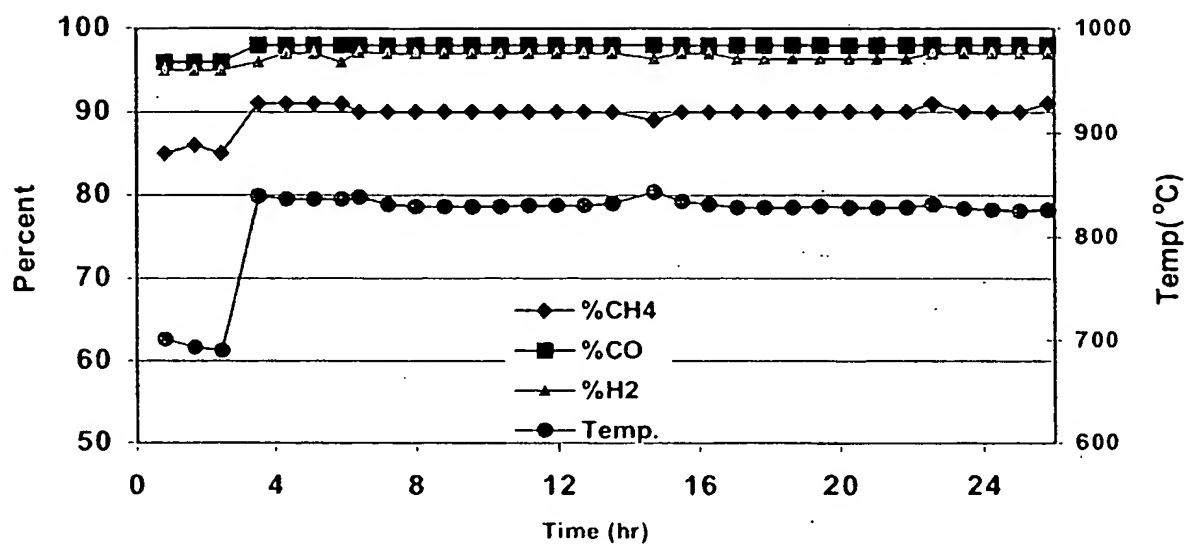


FIG. 1

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 August 2001 (23.08.2001)

PCT

(10) International Publication Number
WO 01/60515 A3

(51) International Patent Classification⁷: B01J 37/02.
35/04, C01B 3/40, 3/38

(21) International Application Number: PCT/US01/05109

(22) International Filing Date: 16 February 2001 (16.02.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/183,576 18 February 2000 (18.02.2000) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
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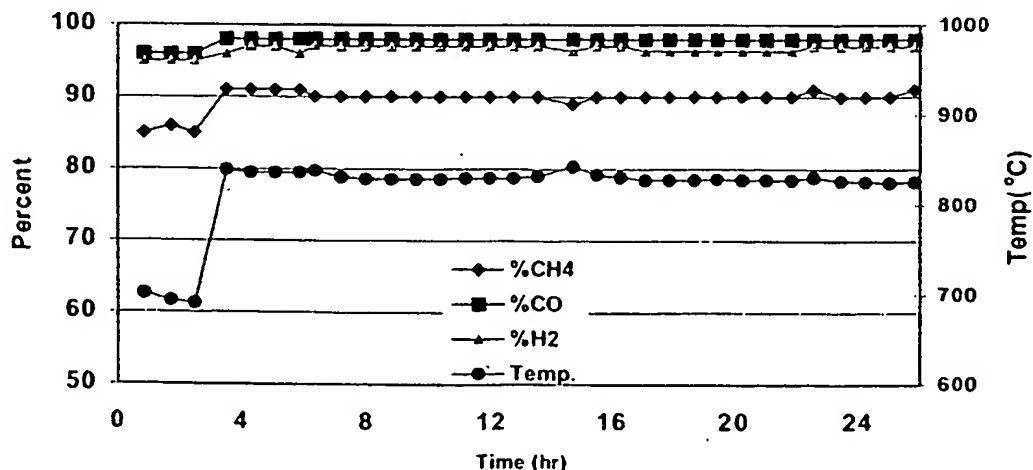
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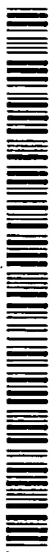
(88) Date of publication of the international search report:
25 April 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: RETICULATED CERAMIC FOAM CATALYSTS FOR SYNTHESIS GAS PRODUCTION



(57) Abstract: Reticulated ceramic monolithic catalysts and non-poisoning catalyst supports comprising one or more metal oxides of chromium, cobalt, nickel, an alkaline earth, a rare earth, or another sinterable metal oxide that are active in any of various chemical oxidation reactions are disclosed. Methods of making the new reticulated ceramic structures comprising impregnating an organic foam or other pore-templating material are also disclosed. Processes for the catalytic conversion of light hydrocarbons to products comprising carbon monoxide and hydrogen employing reticulated ceramic catalysts are described.



WO 01/60515 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/05109

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J37/02 B01J35/04 C01B3/40 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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Date of the actual completion of the international search

31 August 2001

Date of mailing of the international search report

07/09/2001

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International Application No
PCT/US 01/05109

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